DEPARTMENT OF DEFENCE
DEFENCE SCIENCE & TECHNOLOGY ORGANISATION

DSTO

The Effect of FM-73 Cure Temperature on the Durability of Bonded Joints Employing BR127 Primer

Andrew Rider and Peter Chalkley

DSTO-TR-1057

The Effect of FM-73 Cure Temperature on the Durability of Bonded Joints Employing BR127 Primer

Andrew Rider and Peter Chalkley

Airframes and Engines Division
Aeronautical and Maritime Research Laboratory

DSTO-TR-1057

ABSTRACT

Bonded repairs to aircraft structure employing composite patches, may generate significant levels of residual stress in the repaired structure. This is due to the difference in the coefficient of thermal expansion between the repair material and the parent structure. One way of minimising the level of residual stress is to cure the repair adhesive at the lowest possible temperature. FM-73 is a fracture tough adhesive used in bonded repairs that is typically cured at 120°C for 1 hour. However, a cure cycle of 80°C for 8 hours may be employed in critical applications. The durability of bonds formed between aluminium and FM-73 epoxy adhesive using the two cure cycles mentioned has been examined. Al-2024 T3 unclad alloy was pretreated either using the RAAF standard gritblast and silane process or with the gritblast silane process followed by application of BR-127 chromate primer. Results suggest that whilst the addition of BR-127 primer improves bond durability for the adhesive cured at 120°C, there is little improvement observed for the adhesive cured at 80°C. Fracture analysis of failed wedge samples using SEM and surface analysis equipment indicate a change in the locus of fracture for the two cure cycles employed and a possible change in the fracture mechanism. Analysis of bonded samples in cross-section suggest that the interfacial region is wider for the 120°C cured sample. This result may suggest that processes such as interdiffusion of the primer and adhesive layers are important factors governing bond durability of adhesive joints.

RELEASE LIMITATION

Approved for public release

DEPARTMENT OF DEFENCE
DEFENCE SCIENCE & TECHNOLOGY ORGANISATION
DSTO

Published by

DSTO Aeronautical and Maritime Research Laboratory
PO Box 4331
Melbourne Victoria 3001 Australia

Telephone: (03) 9626 7000
Fax: (03) 9626 7999

AR-011-600
October 2000

APPROVED FOR PUBLIC RELEASE

The Effect of FM-73 Cure Temperature on the Durability of Bonded Joints Employing BR127 Primer

Executive Summary

Bonded repairs have been successfully used by RAAF for many years to reduce the cost of maintaining aircraft and to increase aircraft availability. These repairs are often applied using an adhesive which cures at 120°C, however, in some cases a lower cure temperature of 80°C is required. A reduction in cure temperature may affect important properties of the adhesive joint such as strength and durability, and this work was undertaken to see if a cure temperature of 80°C would adversely affect repairs made with FM-73 adhesive and BR-127 primer.

Work presented in this report examined the durability of adhesive joints made using Al-2024 unclad alloy and FM-73 adhesive. The cure cycles investigated were 120°C for 1 hour and 80°C for 8 hours. The aluminium was pretreated using the standard RAAF C5033 gritblast and silane method. The gritblast and silane pretreated surface was also coated with a chromate containing primer layer in some experiments to assess if the primer improved bond durability using the two cure conditions.

Results indicate that the addition of BR-127 primer to a gritblast and silane treated aluminium surface improves bond durability when the FM-73 adhesive is cured at 120°C for 1 hour. In contrast, the primer treated samples bonded with FM-73 cured at 80°C for 8 hours showed no discernible improvement, relative to the standard gritblast and silane pretreatment. The bond durability of the samples prepared with FM-73 cured at 80°C for 8 hours was also poorer in comparison with the samples prepared using the standard cure. Fracture analysis of the gritblast and silane treated samples indicated that the locus of fracture shifted from within a weakened hydrated oxide layer for the 80°C cure to the interfacial region between the adhesive and metal oxide sample for the 120°C cure. Changes in the adhesive fracture surface appearance were indicative of a change in the failure mechanism for the samples cured using the two cycles.

This work has shown that the durability of repairs made with FM-73 adhesive and BR-127 primer after an 80°C cure is lower than that attained after the normal 120°C cure. Durability does not meet the C5033 criteria and use of this cure condition should only be made with engineering advice. The increased understanding gained from this work suggests process improvements which may enable increased durability at the lower temperature cure. This will form the basis of future work.

Authors

Andrew Rider
Airframes and Engines Division

Andrew Rider joined Airframes and Engines Division at DSTO in 1988 as a Professional Officer Class 1. He has a Bachelor of Applied Science in Chemistry from Swinburne University of Technology and a PhD in Physical Chemistry from the University of New South Wales. He is currently employed as a Professional Officer Class 2 and works within Airframes and Engines Division. He is involved in research to understand degradation mechanisms involved in bonded structure and repairs used on F-111 and F/A-18 fighter aircraft.

Peter Chalkley
Airframes and Engines Division

Peter Chalkley is a Senior Professional Officer at AMRL and has a B.Sc (Hons) in Metallurgy from the University of New South Wales and a M.Sc. in Mathematics from Melbourne University and is currently a member of the Australian Composites Structures Society. He joined AMRL in 1986 and has worked on the materials science of adhesives and composite materials.

Contents

1. Introduction

Bonded repairs to Aircraft structure conducted by RAAF adopt the methodology prescribed in Engineering Standard C5033 [1]. This documents details engineering principles employed for bonded repairs including the critical areas of surface pretreatment and cure conditions required for successful and reliable bonding. In some situations the standard cure cycle recommended for a particular adhesive may not be suitable, given high temperature curing can lead to unacceptably high levels of thermally induced residual stresses in the aircraft structure. This is due to the difference in the coefficient of thermal expansion between the repair material and the parent structure. One method of reducing the thermally induced residual stresses is to cure the adhesive at a lower temperature over an extended period. When FM-73 is employed for bonded repairs, a non standard cure cycle of 80^{0}C held for 8 hours may be used instead of the recommended 120^{0}C for 1 hour cure. There is a large durability database available for FM-73 cured using the recommended conditions. A large number of tests conducted by AMRL have clearly established durability performance expected for the standard cure condition. In contrast, there is little information available for the durability of FM-73 adhesive bonds formed using the 80^{0}C for 8 hours cure.

The C5033 RAAF Engineering Standard currently employs a grit-blast silane treatment for repairs with epoxy adhesive and aluminium. The durability performance of the treatment, termed "The Australian Silane Treatment", may be improved by the application of an epoxy primer containing strontium chromate pigments, with a proprietary name of BR-127 [2] [3]. The chromate primer may offer enhanced corrosion resistance for adhesive bonds exposed to harsh environmental conditions and may be employed for critical repairs.

Work presented in this report details bond durability measurements examining the performance of joints made with Al-2024 T3 unclad aluminium and FM-73 cured at 80^{0}C for 8 hours. The surface pretreatments of the aluminium are based on the RAAF standard grit-blast and silane pretreatment [1] followed by application of the BR-127 chromate primer and are detailed in section 2.1. The relative performance of the durability samples cured with the 80^{0}C and 8 hour cycle are compared with similar samples cured with the recommended 120^{0}C and 1 hour cure cycle. The experiments aim to establish if the BR-127 primer improves bond durability for the non standard 80^{0}C and 8 hour cure. Some insight into the mechanism of the BR-127 primer in improving bond durability is provided by surface studies of the adhesive joints and failure surfaces resulting from the bond fracture samples.

The format of the report details the Surface Treatments in Section 2, Experimental Methods in Section 3, Durability Results in Section 4, Fracture Analysis in Section 5, Cross-Sectional Analysis in Section 6, followed by Discussion, Conclusions and Future Work in Sections 7, 8 and 9.

2. Surface Pretreatments

2.1 The Gritblast and Silane Pretreatment of Aluminium

Adherend:

Unclad Al-2024 T3 adherends were employed for all bond fabrication to simulate in service structure which may have been heavily abraded over time to remove the clad protective layer. The aluminium was treated in the following manner:

Solvent Wiping:

Single wiping of the aluminium surface used Methyl Ethyl Ketone (MEK) soaked lanoline and lint free tissues. A fresh tissue was used after each pass. Single wiping was conducted along the grain direction and at 90^0 relative to the grain until no debris or staining of the tissue could be observed.

Scotchbrite Abrasion:

Following solvent wiping the surface was abraded with a Scotchbrite pad soaked in distilled water along the grain direction and at 90^0 relative to the grain until a uniform surface appearance was observed. Single wiping of the aluminium surface then used distilled water soaked lanoline and lint free tissues. A fresh tissue was used after each pass. Wiping was conducted in the direction of the abrasion until no presence of debris or staining of the tissue could be observed. Cleanliness was verified with a water break free surface. The surface was then heated at 110^0C for 15 minutes prior to gritblasting.

Gritblasting:

Uniform gritblasting of the surface employed 50μm alumina grit and dry nitrogen propellant with a pressure of 450kPa and a working distance of 15 to 20cm.

Silane Treatment:

A 1% aqueous solution of γ-glycidoxypropyltrimethoxysilane was stirred for 1 hour prior to commencing the surface pretreatment steps listed above. Distilled water was used to prepare the silane solution. The gritblasted aluminium surface was immersed in the silane solution for 15 minutes and removed and allowed to drain free of excess solution, followed by drying in a 110^0C oven for 60 minutes.

2.2 The BR-127 Primer Pretreatment of Aluminium

The Cytec chromate primer, BR-127, was applied after the silane treatment using an Airbrush with 30psi nitrogen pressure and a working distance of 15 to 20cm. The coating was considered thick enough when a uniform translucent straw colour could just be observed on the gritblasted and silane treated surface. The primer layer was allowed to dry at room temperature for 30 minutes and then heated either to 80^0C or

120^{0}C for 30 minutes. The manufacturer's recommended cure of the BR-127 primer is 30 minutes at room temperature followed by 30 minutes at 120^{0}C.

2.3 FM-73 Cure Conditions

Standard cure of the Cytec FM-73 adhesive used the manufacturer's recommended conditions of 45psi and 120^{0}C for 1 hour. The non-standard cure used 45 psi at 80^{0}C for 8 hours.

3. Experimental Methods

3.1 Environmental Exposure

Bonded test specimens of two types were loaded in mode 1 and exposed to a humid environment of 50^{0}C and 100% relative humidity (R.H.) in an isothermal environmental chamber. Cracklength as a function of time was measured for a period of up to 1000 hours to establish relative durability performance and equilibrium fracture toughness in the humid environment, G_{Iscc}.

3.2 Long Crack Extension (LCE) Test

A Lockheed standard (derived from ASTM D3433: "Fracture strength in Cleavage of Adhesives in Bonded Joints"[4], ASTM D3762: "Adhesive Bonded Surface Durability of Aluminium" [5] and Boeing Spec BSS 7208 [6]) was employed to determine G_{Iscc} for the adhesive joints bonded with FM73 and cured using the two cycles detailed above. The Boeing specimen is the industry accepted specimen, however, the Lockheed sample provides similar results. The dimensions of the test specimen are provided in Figure 1. The thick adherend enables fracture to propagate in the adhesive without problems associated with plastic yielding of the aluminium that may be encountered with thinner samples. (A 3mm thick adherend, as used in wedge tests, may deform plastically due to the high fracture toughness of the FM-73 adhesive [7]). A longer initial cracklength also reduces errors in calculation of G_1 [8]. After bolt loading the sample, crack growth was allowed to equilibrate at ambient conditions over several hours prior to insertion in the humid environment.

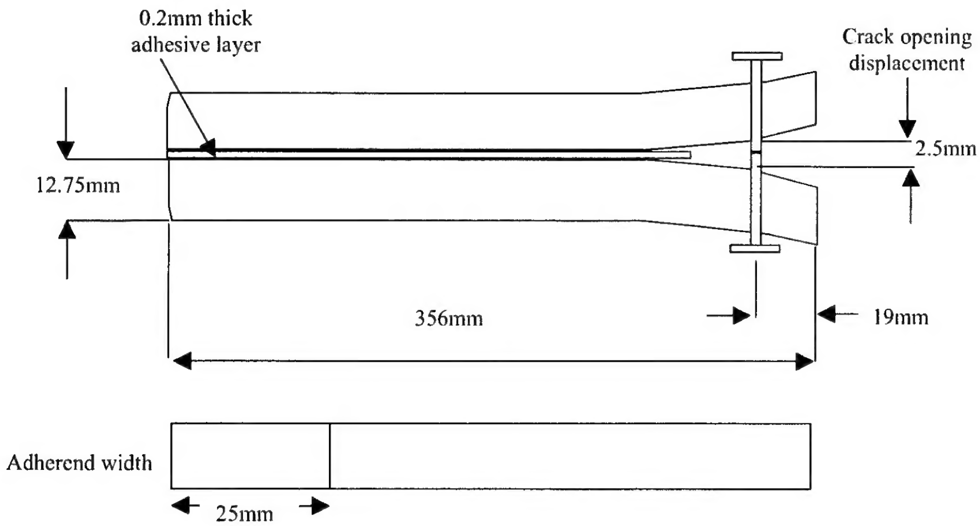

Figure 1 Long crack extension test sample dimensions

3.3 Boeing Wedge Test Durability Sample

The Boeing Wedge test durability sample was employed to provide qualitative durability data which may be compared with the fracture toughness information derived from the long crack extension test, described in section 3.2. The wedge test is used qualitatively and, due to cheaper production, may be destructively tested to establish modes of bond failure. The wedge test was performed in accordance with ASTM D-3762 [5]. The sample dimensions were 150mm long by 25mm wide using 3.18mm thick adherends with a crack opening displacement of 3.18mm. The wedge was inserted using a drill press under constant load and the crack growth was allowed to equilibrate at ambient conditions over several hours prior to insertion in the humid environment.

3.4 Fracture Analysis

The failure surfaces of durability samples that had been prepared with the 80^{0}C and 120^{0}C FM-73 cure cycles, were analysed using X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM). XPS was performed by irradiating samples with a 150W AlK_α flux in a vacuum of $5x10^{-9}$ torr. Photoelectrons were analysed with a Fixed Retard Ratio of 24 and binding energy was referenced to the adventitious C 1s line at 285eV. Quantification used sensitivity factors provided by the manufacturer. SEM was performed with a 20kV electron beam on samples coated with a 0.5µm layer of sputtered gold.

XPS analysis provided chemical information emanating from the first 5nm of the fracture surface and SEM micrographs provided visual details of the humid fracture process.

3.5 Cross Sectional Analysis of Chromate Primer Treated Samples

The distribution of the chromate primer in the interfacial layer between the adhesive and aluminium substrate was examined using two methods. In the first experiment, bulk samples of lightly gritblasted and primer treated aluminium surfaces, that were bonded with FM-73 using the two cure cycles, were polished metallographically in cross-section. The samples were carbon coated with a 500nm thick film and analysed with SEM. Micrographs recorded with secondary electrons were used to examine morphological differences present in the interfacial region. Micrographs recorded with backscattered electrons were used to identify compositional differences in the interfacial region. In a second experiment aluminium coupons that were milled to produce a contaminant free mirror-finish [9] were treated with silane and BR-127 primer, as described in section 2. A 500nm thick microtomed cross-section was analysed with an electron microprobe in the interfacial region to measure the chromium distribution for the samples bonded with FM-73 using the 120°C or 80°C cure cycles.

Application of the primer to the metal surfaces was performed to insure that the primer thickness on the 120°C and 80°C FM-73 cured samples was as similar as possible. This was achieved by spraying the metallic surface with primer and cutting aluminium coupons from adjacent regions. The primer was applied on separate occasions for the two experiments and some variation between experiments may be expected, however, the primer thickness of the 120°C and 80°C sample pairs would be expected to be identical.

4. Durability Results

4.1 LCE Results

4.1.1 LCE results for FM73 cured at 120°C

Figure 2 shows the fracture toughness values, G_1 (J/m^2), measured for Al-2024 T3 unclad aluminium bonded with FM-73 that was cured at 120°C for 1 hour. The pretreatments are indicated in the legend. G_I was calculated using equation 1.

$$G_I = \frac{Y^2.E.h^3\left[3(a+0.6h)^2+h^2\right)]}{16\left[(a+0.6.h)^3+a.h^2\right]^2} \qquad (1)$$

where Y is the crack opening displacement, h is the adherend thickness, E is Young's modulus and a is cracklength. The data indicates two effects. The addition of the BR-127 primer improves the equilibrium fracture toughness, G_{Iscc} of the gritblast and silane treatment by approximately 600J/m² at 1000 hours exposure. Curing the primer either at 120°C or 80°C appears to produce a similar durability performance for the adhesive joint.

4.1.2 LCE results for FM73 cured at 80°C

Figure 3 shows the fracture toughness values, G_I (J/m^2), measured for Al-2024 T3 unclad aluminium bonded to FM-73 that was cured at 80°C for 8 hours. The pretreatments are indicated in the legend. G_I was calculated using equation 1. In contrast with the data shown in Figure 2, there does not appear to be any improvement in bond durability offered by using the BR-127 primer in addition to the standard grit-blast and silane treatment. The range of primer cure conditions examined also suggests that primer curing is not a critical property affecting the joint fracture toughness. The comparison of the 120°C cure and 80°C cure fracture toughness data in Figures 2 and 3 also indicates the silane treatment is not as durable in the 80°C cure sample. The range of G_I values at 1000 hours for silane alone is 550-750J/m^2 for the 120°C cure and 300-500 J/m^2 for the 80°C cure. The G_I fracture values measured prior to exposure to the high humidity environment also indicate, on average, lower values for the 80°C cure samples.

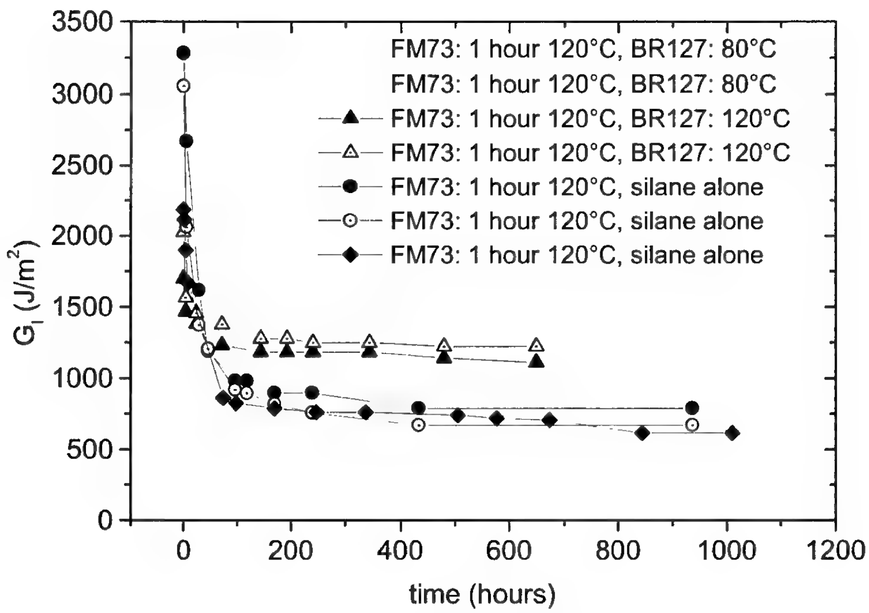

Figure 2. G_{Iscc} for LCE adhesive joints prepared with FM73 cured at 120°C. The data indicates the relative effect of the primer and its cure on bond durability.

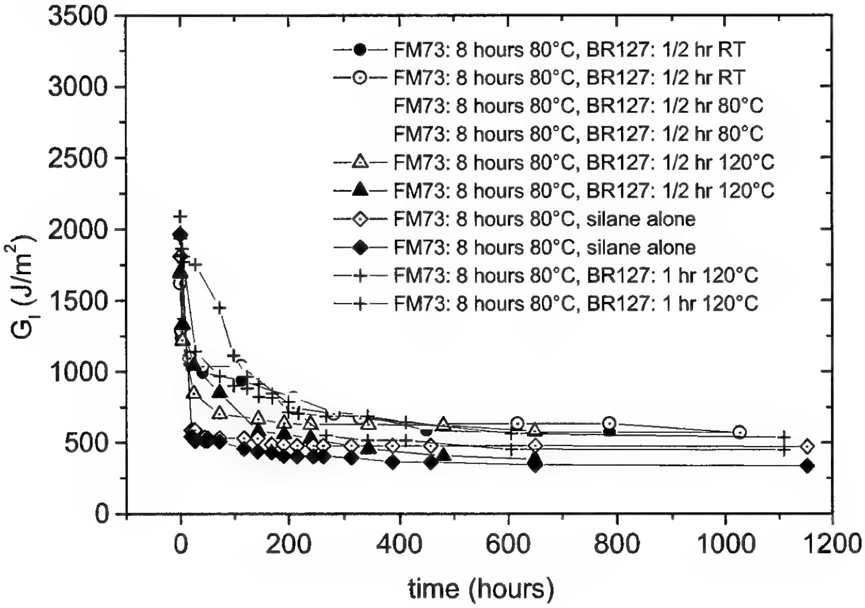

Figure 3. G_{Iscc} for LCE adhesive joints prepared with FM73 cured at 80°C. The data indicates the relative effect of the primer and its cure on bond durability.

4.2 Boeing Wedge Test (BWT) Results

4.2.1 BWT results for FM73 cured at 120°C

Figure 4 indicates the relative durability for Al-2024 T3 clad aluminium wedge samples bonded with FM-73 cured at 120°C for 1 hour. The data shows a qualitative difference in durability for the silane and BR-127 primer pretreated samples, similar to the data presented in Figure 2. Clearly, the additional primer treatment improves the bond durability performance in a 50°C humid environment. The wedge data also suggests that the failure analysis of these wedge samples would be representative of the failure modes which would be expected for the LCE samples in Figure 2.

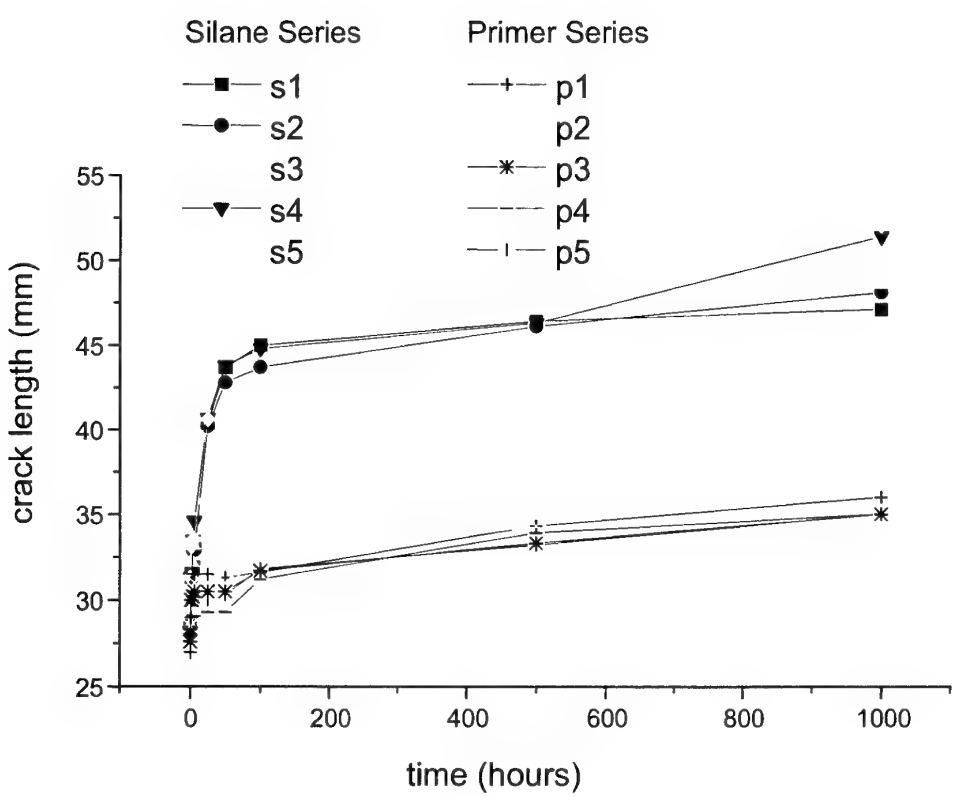

Figure 4 *The relative durability for Al-2024 T3 clad aluminium wedge samples bonded with FM-73 at 120⁰C for 1 hour. The superior performance of the primer treated samples relative to the silane only treated samples is apparent.*

4.2.2 BWT results for FM73 cured at 80°C

Figure 5 shows the relative durability for Al-2024 T3 clad aluminium wedge samples bonded with FM-73 cured at 80⁰C for 8 hours. The data shows similar durability for the silane and BR-127 primer pretreated samples, similar to the data presented in Figure 3. The additional primer treatment has little influence on the bond durability performance in a 50⁰C humid environment. The wedge data suggests that the failure analysis of these wedge samples would be representative of the failure modes expected for the LCE samples in Figure 3. In contrast to the data shown in Figure 4, there is a larger degree of scatter for the cracklength values in Figure 5. The greater scatter may suggest greater variation in the formation of durable adhesive bonds for the 80⁰C cure condition.

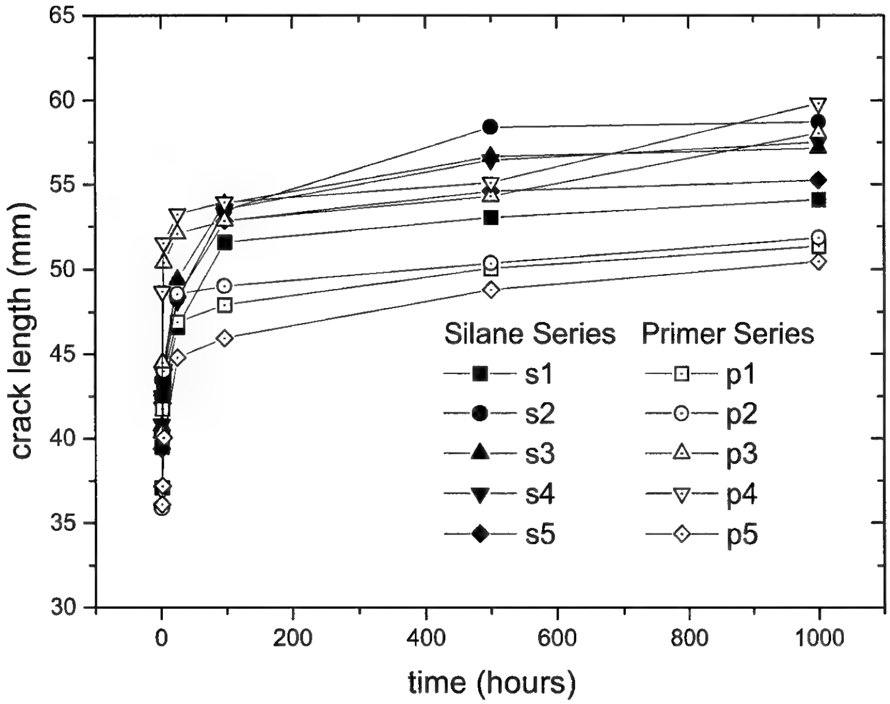

Figure 5 *The relative durability for Al-2024 T3 clad aluminium wedge samples bonded with FM-73 at 80°C for 8 hours. The performance of the silane and primer treated samples is relatively similar.*

5. Fracture Analysis

Given the wedge test data indicated similar behaviour to the results observed for the LCE samples, fracture analysis of the failed wedge samples should provide information about the bond degradation mechanisms.

5.1 XPS Fracture Analysis

Table 1 provides the atomic concentrations of elements detected on the fracture surfaces of the samples prepared with FM-73 adhesive cured at 120°C. The "adhesive" side represents the fracture surface which retained the FM-73 layer, whereas the "metal" side represents the fracture surface of the adherend with a metallic appearance.

Table 2 provides the atomic concentrations of elements detected on the fracture surfaces of the samples prepared with FM-73 adhesive cured at 80°C.

Table 1 indicates that for the 120°C FM-73 cured, silane treated sample, fracture propagates near the adhesive-oxide interface. The presence of aluminium, silicon and

nitrogen on both fracture surfaces indicates the fracture moves between the silane-adhesive layer and into the aluminium oxide. Addition of the chromate primer appears to shift the fracture path more along the interface between the silane and primer layer, away from the oxide-silane interface.

Table 1 XPS fracture analysis of failed wedge samples prepared with FM-73 cured at 120°C for 1 hour and 45 psi.

Treatment	Fracture Surface	Atomic Concentration (%)						
		Al	Si	C	N	O	Cr	Na
Silane	adhesive	3.9	5.9	58.1	1.1	30.2	---	0.8
Silane	metal	16.2	4.6	32.4	0.6	45.2	---	0.9
BR-127	adhesive	0.3	5.0	60.9	1.2	31.6	0.6	---
BR-127	metal	9.4	2.9	35.9	---	50.2	1.6	---

Table 2 XPS fracture analysis of failed wedge samples prepared with FM-73 cured at 80°C for 8 hours and 45 psi.

Treatment	Fracture Surface	Atomic Concentration (%)						
		Al	Si	C	N	O	Cr	Na
Silane	adhesive	15.6	0.2	35.7	1.0	45.9	---	1.7
Silane	metal	27.9	0.3	10.8	---	60.7	---	---
BR-127	adhesive	9.5	3.5	40.4	2.7	42.1	1.8	---
BR-127	metal	19.1	1.5	25.0	1.4	52.2	0.8	---

Table 2 indicates differences in the fracture surfaces for the 80°C cured samples, relative to the 120°C cured samples in Table 1. The 80°C cured, silane treated sample indicates a large percentage of fracture propagates within the oxide layer. Evidence for this fracture path is provided by the 16 atomic percent of aluminium present on the "adhesive" surface, the small silicon concentrations of both fracture faces and the diminished carbon concentration on the "adhesive" surface relative to the 120°C cured sample in Table 1. In contrast with the 120°C cured sample, addition of the chromate primer for the 80°C cured sample does not appear to significantly alter the fracture path. The presence of 10 atomic percent of aluminium on the "adhesive" surface indicates that a substantial amount of fracture still propagates through the aluminium oxide layer. The increased levels of silicon and the presence of nitrogen and chromium, however, do suggest that some fracture is propagating at the primer-silane interface. The smaller chromium signal on the metal surface indicates that fracture is closer to the silane-oxide layer than the primer-adhesive interface, as was the case for the 120°C cured sample.

In summary, fracture in the 120°C cured sample appears to propagate mainly at the adhesive-silane and adhesive-primer interfaces for the silane and BR-127 treated samples, respectively. In the case of the 80°C cured samples, fracture propagates predominantly within the aluminium oxide layer for the silane and primer treated samples. The addition of the primer layer moves a small proportion of fracture into the silane-primer interface.

5.2 SEM Analysis

5.2.1 Gritblast and Silane Treatment

Figures 6 and 7 indicate the "adhesive" and "metal" surfaces of the failed wedge specimen prepared with the gritblast and silane treatment and bonded with FM-73 cured at 120ºC for 1 hour.

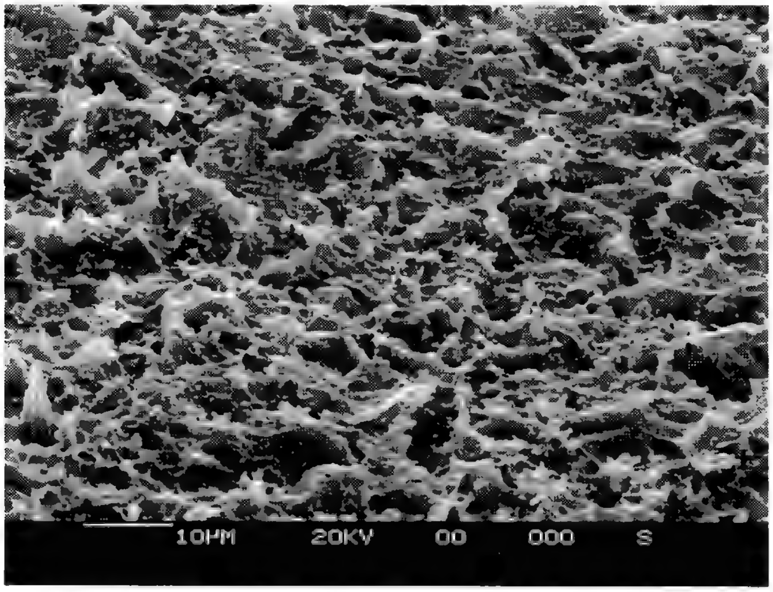

Figure 6 *SEM micrograph of the failed "adhesive" surface of the wedge test sample prepared with the gritblast and silane treatment and cured at 120ºC for 1 hour with FM-73 adhesive. The image was taken at a 40º tilt angle.*

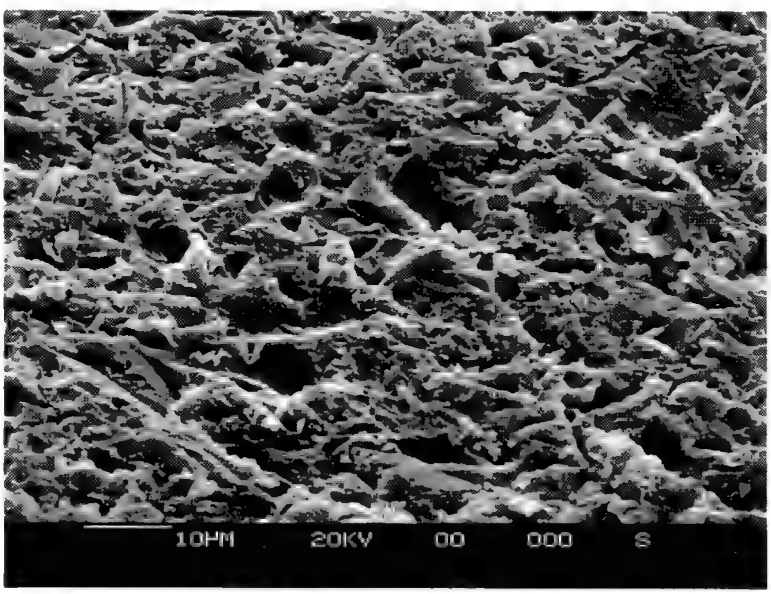

Figure 7 *SEM micrograph of the failed "metal" surface of the wedge test sample prepared with the gritblast and silane treatment and cured at 120ºC for 1 hour with FM-73 adhesive. The image was taken at a 40º tilt angle.*

Figures 8 and 9 indicate the "adhesive" and "metal" surface of the failed wedge specimen prepared with the gritblast and silane treatment and bonded with FM-73 cured at 80⁰C for 8 hours.

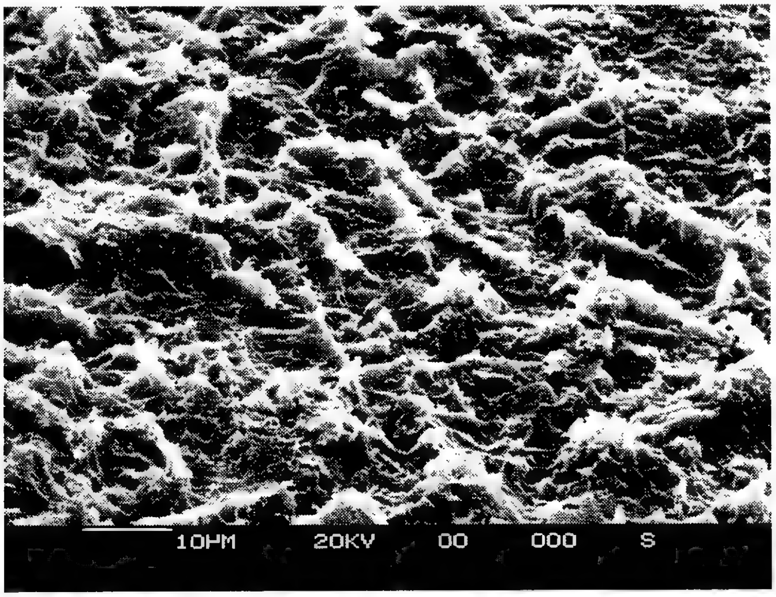

Figure 8 SEM micrograph of the failed "adhesive" surface of the wedge test sample prepared with the gritblast and silane treatment and cured at 80⁰C for 8 hours with FM-73 adhesive. The image was taken at a 40⁰ tilt angle.

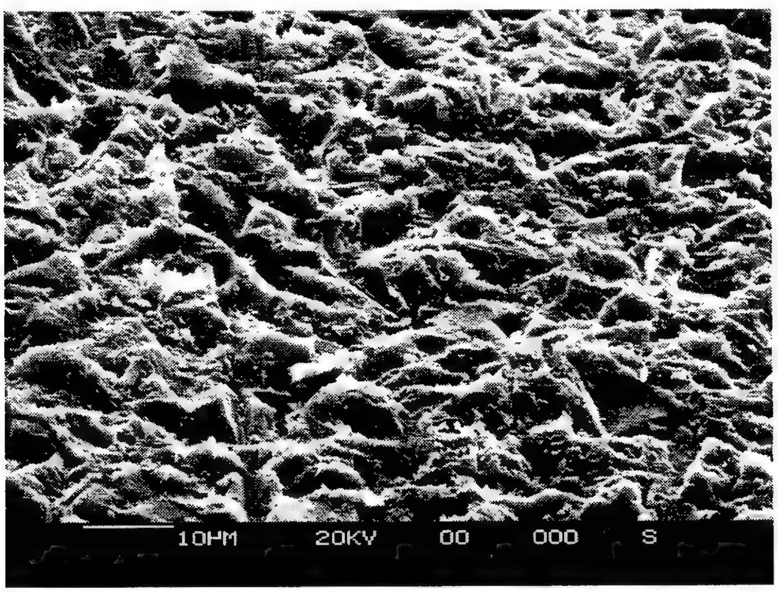

Figure 9 SEM micrograph of the failed "metal" surface of the wedge test prepared with the gritblast and silane treatment and cured at 80⁰C for 8 hours with FM-73 adhesive. The image was taken at a 40⁰ tilt angle.

Figures 6 and 8 show subtle differences between the adhesive fracture surface of the 120⁰C and 80⁰C cured samples. Whilst both images indicate the jagged edges resulting from the adhesive pulling away from the grit-blasted surface, shown in Figures 7 and 9, these features appear to be notably coarser for the 80⁰C cure sample. Given the appearance of the gritblasted "metallic" surfaces for the 80⁰C and 120⁰C

cured samples appear to be similar, it is reasonable to assume that the differences in appearance of the "adhesive" failure surfaces are caused by subtle changes in the fracture mechanism.

5.2.2 Gritblast, Silane and Primer Treatment

Figures 10 and 11 indicate the "adhesive" and "metal" surfaces of the failed wedge specimen prepared with the gritblast, silane and BR-127 primer treatment and bonded with FM-73 cured at 120^{0}C for 1 hour.

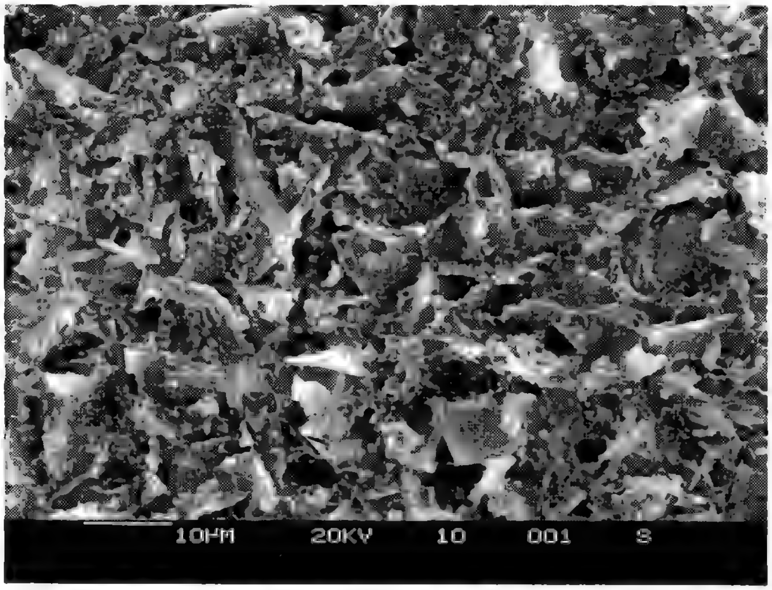

Figure 10 SEM micrograph of the failed "adhesive" surface of the wedge test sample prepared with the gritblast, silane and BR-127 primer and cured at 120^{0}C for 1 hour with FM-73 adhesive. The image was taken at a 0^0 tilt angle.

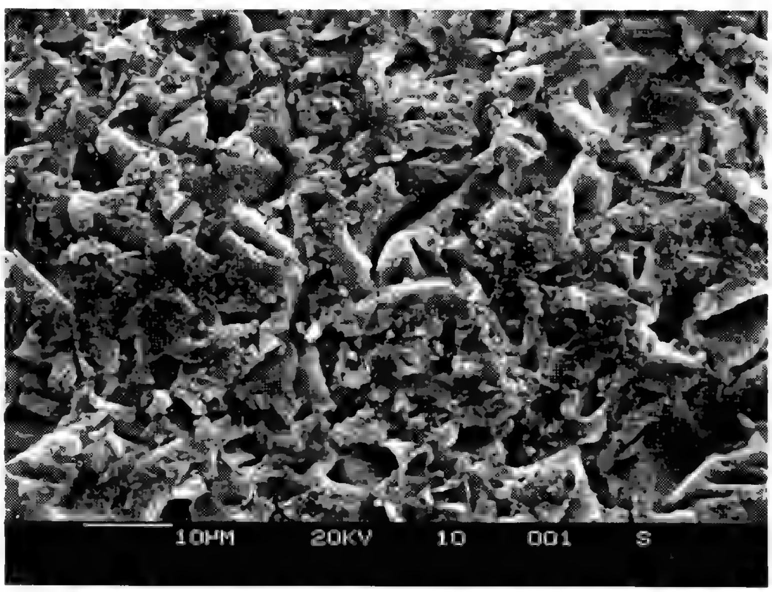

Figure 11 SEM micrograph of the failed "metal" surface of the wedge test sample prepared with the gritblast, silane and BR-127 primer and cured at 120^{0}C for 1 hour with FM-73 adhesive. The image was taken at a 0^0 tilt angle.

Figures 12 and 13 indicate the "adhesive" and "metal" surfaces of the failed wedge specimen prepared with the gritblast,silane and BR-127 primer treatment and bonded with FM-73 cured at 80^0C for 8 hours.

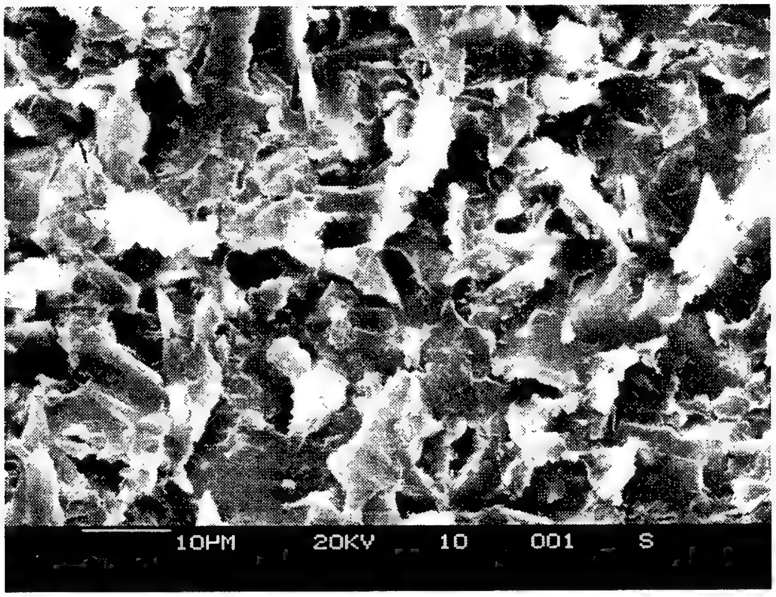

Figure 12 SEM micrograph of the failed "adhesive" surface of the wedge test sample prepared with the gritblast, silane and BR-127 primer treatment and cured at 80^0C for 8 hours with FM-73 adhesive. The image was taken at a 0^0 tilt angle.

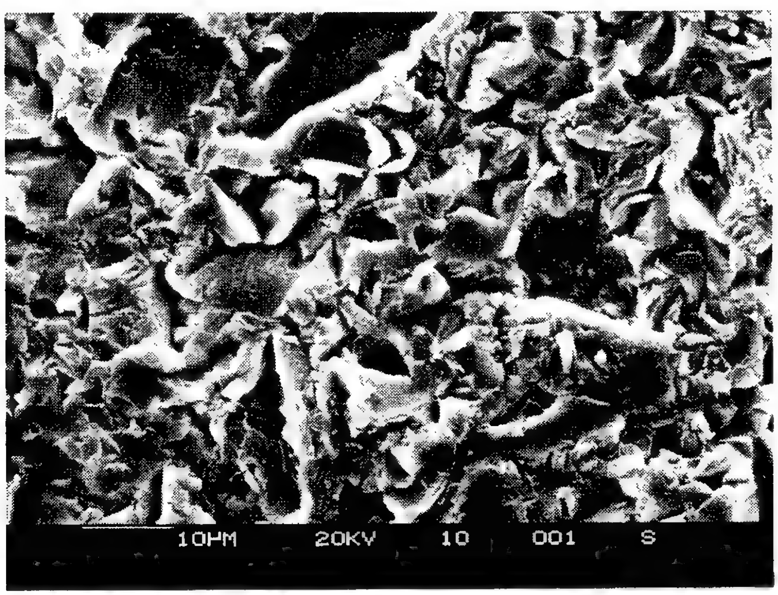

Figure 13 SEM micrograph of the failed "metal" surface of the wedge test sample prepared with the gritblast, silane and BR-127 primer treatment and cured at 80^0C for 8 hours with FM-73 adhesive. The image was taken at a 0^0 tilt angle.

Figures 11 and 13 indicate gritblasted surface features with similar dimensions. The "adhesive" failure surfaces shown in Figures 10 and 12 indicate coarser surface features for the FM-73 80^0C cured sample. This trend was also observed for the silane treated fracture samples in section 5.2.1. The fracture images in sections 5.2.1 and

5.2.2, suggest that the failure mechanism for the 120°C and 80°C cured adhesive wedge test samples have subtle differences.

6. Cross-Sectional Analysis

Figure 14 indicates an SEM image of gritblasted, silane and primer treated aluminium bonded to FM-73 cured at 120°C for 1 hour that had been polished in cross-section. The micrograph indicates an interphase zone approximately 17μm in width between the metal and adhesive regions. Within this region are Strontium Chromate pigments which are highlighted in the backsattered image in Figure 15. The backscattered image may indicate a subtle change in contrast of the interphase zone, compared with the bulk adhesive. Figure 14 and 15 both indicate that the interphase region is wider than the area occupied by the Strontium Chromate pigments. Measurements taken at several positions along the interphase region indicate a typical width of 17μm and the zone containing the pigments is approximately 13μm wide.

Figures 16 and 17 indicate the secondary electron and backscattered images acquired for the polished cross-sections of the gritblasted, silane and primer treated aluminium sample bonded to FM-73 for 8 hours at 80°C. Figures 16 and 17 do not exhibit a distinctive interphase region that was observed for the 120°C cured sample. Whilst close inspection reveals a fine line between the primer layer and the adhesive, this layer appears to trace the outline of the Strontium Chromate pigments and does not extend past the pigment layer as was observed for the 120°C cured sample. Measurements taken at several positions along the interphase region indicate a typical width of 10μm. Therefore, the width of the interphase region for the 80°C cured sample is notably lower than the 120°C cured sample.

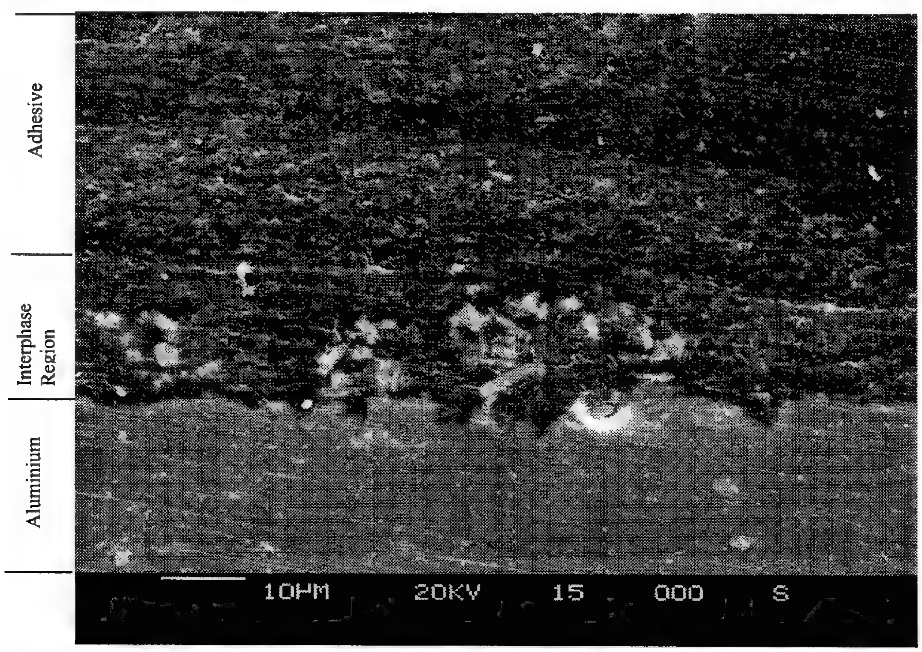

Figure 14 SEM image of a polished aluminium cross-section that had been gritblasted, silane and primer treated and bonded to FM-73 cured at 120°C for 1 hour.

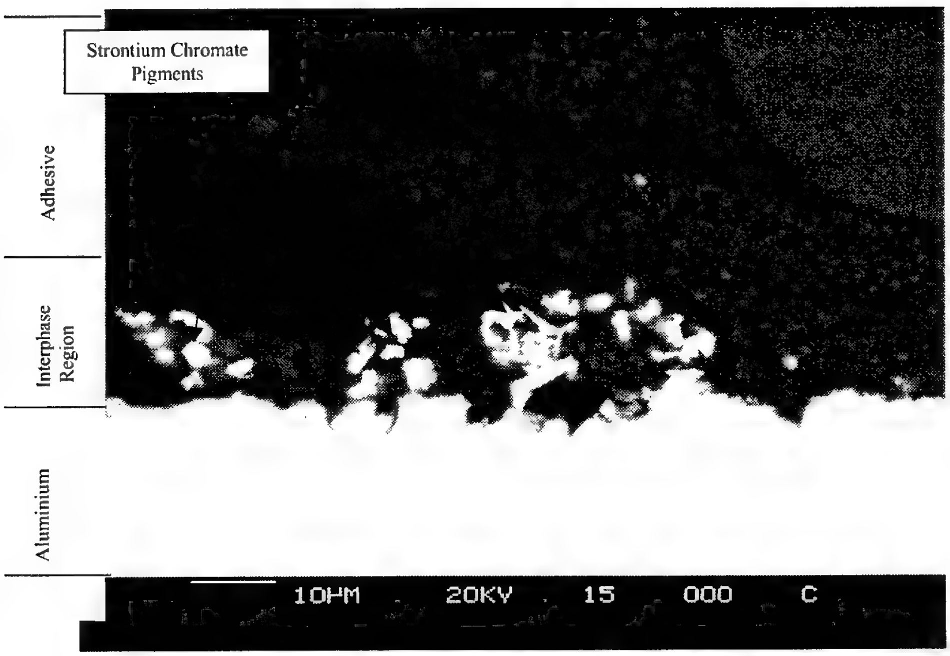

Figure 15 Backscattered electron image of a polished aluminium cross-section that had been gritblasted, silane and primer treated and bonded to FM-73 cured at 120°C. Same field of view as Figure 14.

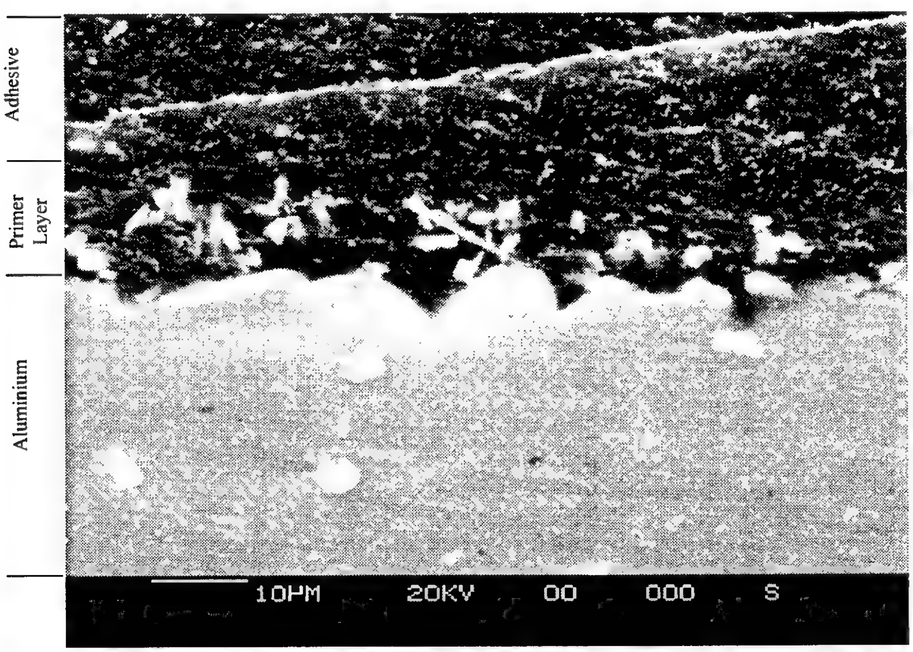

Figure 16 SEM image of a polished aluminium cross-section that had been gritblasted, silane and primer treated and bonded to FM-73 cured at 80°C for 8 hours.

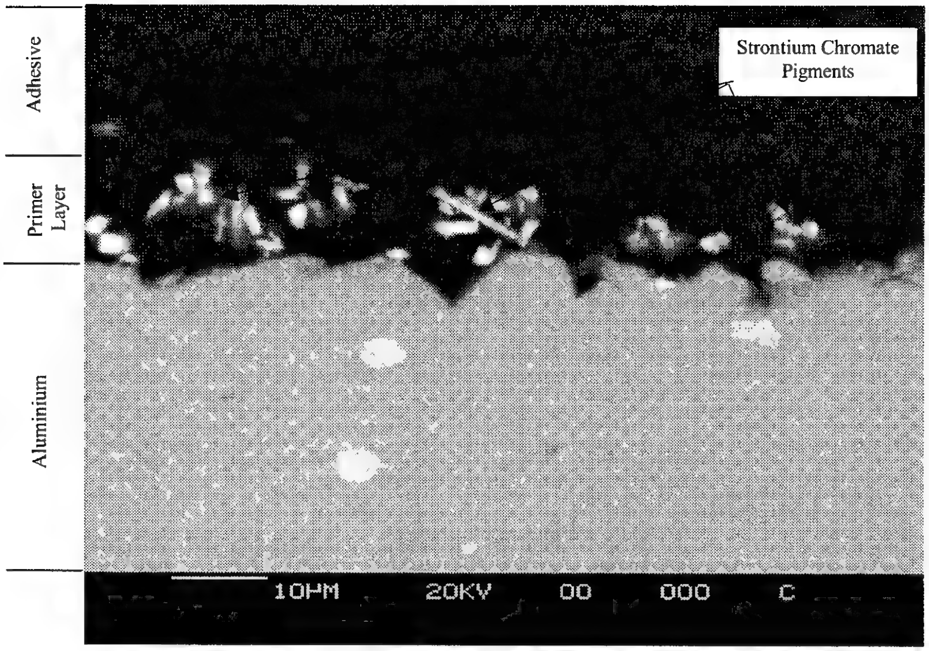

Figure 17 Backscattered electron image of a polished aluminium cross-section that had been gritblasted, silane and primer treated and bonded to FM-73 cured at. 80°C for 8 hours. Same field of view as Figure 16.

Analysis of the primed aluminium samples bonded to FM-73 cured at 120°C and 80°C was also carried out with microtomed cross-sections of 500nm thickness using an electron microprobe. The thin cross-sections were prepared in an effort to improve the spatial resolution of the elemental mapping in the interfacial region of the bonded samples. Figures 18 and 19 show the line profiles generated from chromium and aluminium maps of the samples cured at 120°C and 80°C, respectively. The plots indicate the number of counts, including the background level, for the respective elements as a function of distance from the adhesive layer, to the interfacial region and into the aluminium substrate. The width of the chromium layer for the two samples was approximately 2μm for the 120°C sample and 0.5μm for the 80°C sample, indicated on the plots. The data is consistent with the SEM analysis of Figures 14 to17 and also suggests that the chromium layer is slightly thicker for the FM-73 sample cured at 120°C. The difference in the chromium thickness layer values measured using the two methods is notably different and either represents variation in primer coating thickness for individual applications or differences caused by variation in sample preparation.

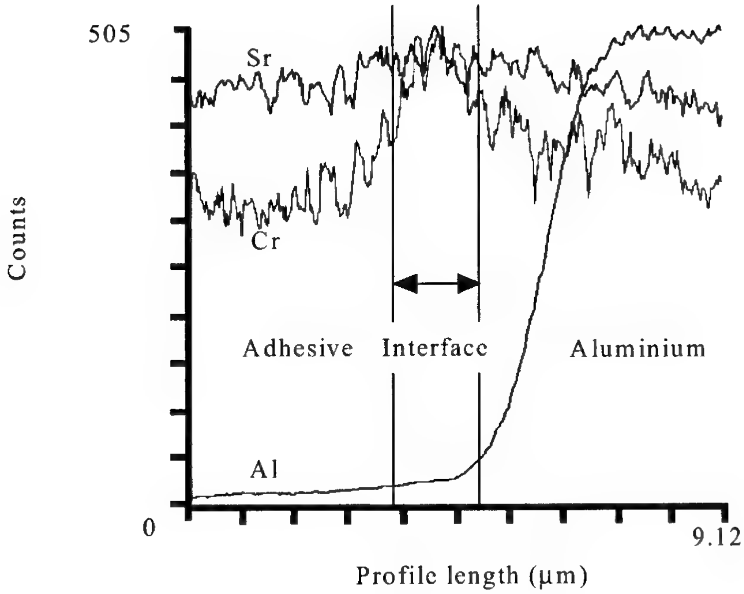

Figure18 Line profiles generated from electron microprobe maps of the microtomed cross-section sample prepared by curing FM-73 at 120°C for 1 hour

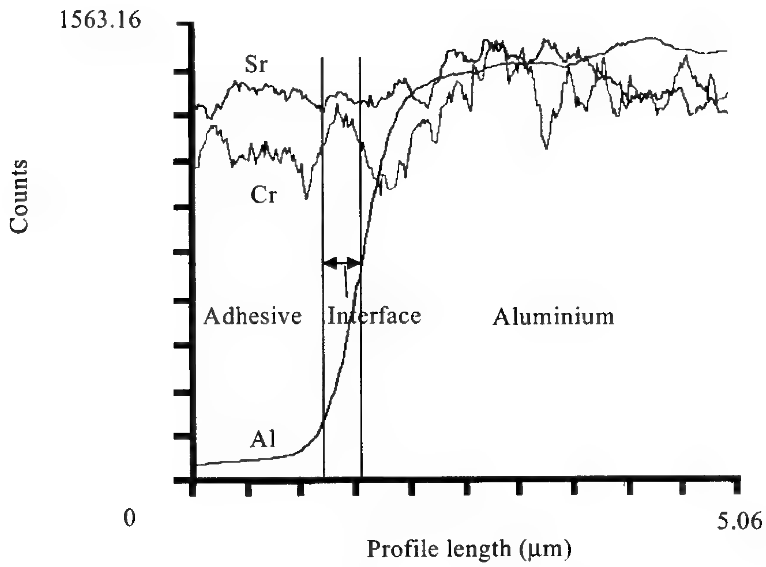

Figure19 Line profiles generated from electron microprobe maps of the microtomed cross-section sample prepared by curing FM-73 at 80°C for 8 hours

7. Discussion

An important feature of the plots displayed in Figures 2 and 3 is that the chromate primer improves the humid fracture toughness of the aluminium-epoxy bond when a standard 120°C and 1hour cure is employed, whereas, the primer appears to have negligible influence on the performance of the aluminium-epoxy bond for the 80°C and 8 hour cure condition. The cure temperature of the primer layer prior to either the 120°C or 80°C adhesive cure also appears to have little influence on the durability performance of the aluminium-epoxy bond. These results may suggest that the reaction between the FM-73 adhesive and the primer layer is dependent on the cure conditions employed for the FM-73 adhesive. The physical properties of the adhesive may also depend on the cure conditions employed. A comparison of different physical properties of the FM-73 adhesive cured under the two conditions is shown in Table 3.

Table 3 Physical properties of FM-73 cured at 120°C for 1 hour and 80°C for 8 hours.

Cure Cycle	T_g (dry/°C)[10]	T_g (wet/°C)[10]	G_{Ic} (J/m^2)[7]	Shear Strength(MPa)[10]
120°C/1 hour	99	83	3000[&]	36[$]
80°C/8 hours	94	81	1172-1646[@]	38[$]

& measured at 21°C for a bondline thickness of 0.2mm

@ measured at 21°C for a bondline thickness of 0.1mm to 0.4 mm

$ measured at 21°C

The values in Table 3 suggest that most of the physical properties of the FM-73 adhesive are relatively similar for the two cure conditions. However, the dry Mode 1 fracture toughness data does indicate that the 80°C cure produces a lower value, consistent with the data presented in Figures 2 and 3. This suggests that the 80°C and 8 hour cure produces an adhesive that is more brittle than the 120°C and 1 hour cure.

Some evidence for a change in the failure mode for the two cure conditions is supported by the surface analysis data (Tables 1 and 2). The 80°C cure samples fail either within a weakened hydrated oxide layer or near the oxide-adhesive interfacial layer. The 120°C cured samples indicate fracture propagates interfacially and into the adhesive layer. SEM images (Figures 6, 8, 10 and 12) indicate that the adhesive fracture surface has coarser features for the 80°C cured samples. As the adhesive joint fails interfacially, stress would be expected to concentrate in the interfacial region between the sharp edges of the gritblasted surface features and the adhesive. Coarser features may suggest reduced wetting of the gritblasted surface by the adhesive in the 80°C and 8 hours cure cycle. Energy dissipation processes in the adhesive, leading to yielding and plastic deformation may also have altered for the two cure cycles examined. In the case of the adhesive cured with the 80°C and 8 hours cycle, coarser features may suggest energy dissipation processes are less uniform and, therefore, less efficient.

The reduction in fracture toughness of the 80°C and 8 hour cured FM-73 adhesive may explain the relative durability performance for the two cure cycles employed, but does not explain the negligible influence of the BR-127 primer on durability

performance of the 80°C and 8 hour cure sample. Interaction between the primer and adhesive layer may be an important process contributing to the formation of strong and durable adhesive bonds.

The Diffusion Theory of Adhesion, has been used to describe the intrinsic adhesion between polymer layers [11]. The theory indicates that adhesion results from the interdiffusion of two polymer layers across the interfacial region. The conditions for good adhesion require the polymer molecules to be mutually soluble and sufficiently mobile to interdiffuse. In the case of bonding FM-73 to the BR-127 layer, both layers are epoxy polymeric material and should interdiffuse on the basis of solubility. The mobility of the two layers will depend on the cure conditions employed and would be important in determining the interfacial adhesion.

Figure 20 plots the viscosity of FM-300 adhesive as a function of the range of temperatures used in these studies [12]. Whilst FM-300 is not identical in nature to FM-73, the two adhesives flow to a similar degree during cure, suggesting both adhesives would have a similar viscosity-temperature relationship. There is approximately a five fold reduction in adhesive viscosity in the temperature range between 80°C and 120°C and may indicate that the reduced viscosity of the FM-73 adhesive is a factor that would influence interdiffusion between the primer and adhesive layers. The mobility of the primer layer would also be an important factor and changes in the BR-127 properties in the 80°C to 120°C temperature should also be examined. Based on the data in Figures 2 and 3, the pre-cure of the primer layer between room temperature and 120°C, does not appear to alter the properties influencing an interdiffusion process.

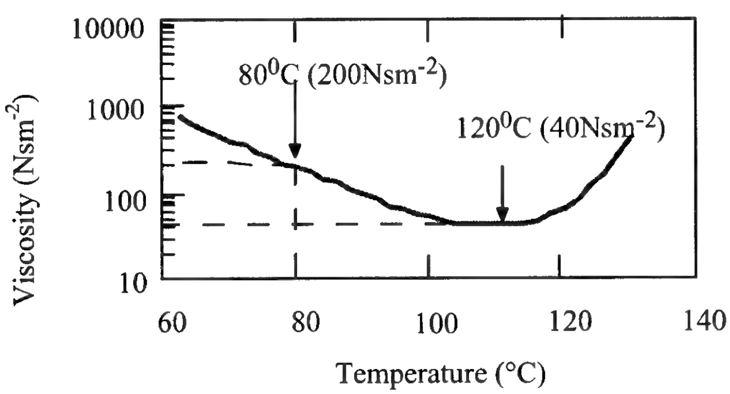

Figure 20 Viscosity of FM-300 adhesive as a function of temperature.

Evidence to suggest that differences in the interfacial region exist for the two cure cycles examined are provided in Section 6. Whilst these results are not conclusive, they do suggest interdiffusion of the primer layer with the adhesive layer may increase for the 120°C cure cycle. This may contribute to the improved durability performance of the primed sample relative to the silane treated sample for the 120°C cure sample.

8. Conclusions

The addition of BR-127 primer to a gritblast and silane treated aluminium surface improves the durability of bonds formed with FM-73 cured at 120°C and 1 hour. In contrast, the chromate primer does not have any influence on the durability of bonds formed with FM-73 cured for 8 hours at 80°C. Cure of the BR-127 layer between room temperature and 120°C for 30 minutes prior to bonding with FM-73 does not influence the durability of the adhesive bond.

FM-73 cured at 80°C for 8 hours has a lower fracture toughness than FM-73 cured at 120°C for 1 hour. Examination of fracture surfaces from failed durability samples indicates that the fracture mechanism alters for the 120°C and 80°C cure cycles. XPS indicates the fracture for the 80°C cure samples propagates between the adhesive-aluminium oxide interface and within a cohesively weakened oxide layer. In contrast, the 120°C cure samples fail predominantly at the adhesive-oxide interface with some failure propagating into the adhesive layer for the primed specimens. SEM analysis of the adhesive fracture surfaces reveal coarser features for the 80°C cure samples. This may suggest either reduced wetting of the gritblasted surface by the adhesive or an alteration in the interfacial energy dissipation mechanisms compared to the 120°C cure samples.

Evidence provided by cross-sectional analysis of the primed samples suggests that the interfacial region is wider for FM-73 cured at 120°C and 1 hour. Interdiffusion between the primer and adhesive layer may be an important process influencing the formation of a durable adhesively bonded joint.

Boeing wedge test experiments, when carried out under strict guidelines, provide qualitative information which is consistent with durability data established from quantitative thick adherend samples. This provides confidence in the use of the wedge test as a quality control tool in adhesive bonding operations.

9. Future Work

Further studies examining the interaction between the primer and adhesive layers during cure need to be undertaken. Mechanisms influencing the performance of the BR-127 primer can provide important information that may enable conditions to be adjusted to optimise bond durability in low cure temperature operations. An initial experiment would be to examine the influence that briefly heating the adhesive to 120°C at the start of the 80°C and 8 hour cure cycle would have on the bond durability performance of the primer treated joint. Time spent at the 120°C temperature would have to be minimised to achieve maximum viscosity and minimum degree of cure.

10. References

[1] Royal Australian Air Force Engineering Standard C5033, "Composite Materials and Adhesive Bonded Repairs" September 1995, RAAF Headquarters Logistics Command, Melbourne, Victoria, Australia

[2] A. A. Baker, R. J. Chester, International Journal of Adhesion and Adhesives, 12, 73, 1992.

[3] A. N. Rider, D. R. Arnott, International Journal of Adhesion and Adhesives, 20, 209, 2000.

[4] ASTM, Annual Book of Standards, Section 15, vol 15.06, Adhesives. Philadelphia: ASTM, 1995-ASTM D3433, "Fracture strength in Cleavage of Adhesives in Bonded Joints".

[5] ASTM, Annual Book of Standards, Section 15, vol 15.06, Adhesives. Philadelphia: ASTM, 1995-ASTM3762, "Adhesive Bonded Surface Durability of Aluminium".

[6] Boeing Aircraft Company, Specification for Adhesive Joint Durability Testing, BSS 7208.

[7] P. D. Chalkley, "A Critical Compendium of Material Property Data for Bonded Composite Repairs", Divisional Discussion Paper, DSTO-DDP-0274, DSTO, 1997.

[8] M. H. Stone, T. Peet, "Evaluation of the Wedge Test for Assessment of Durability of Adhesive Bonded Joints", Royal Aircraft Establishment, Technical Memorandum, Mat 349, July, 1980.

[9] A. N. Rider, C. L. Olsson-Jacques, D. R. Arnott, Surface and Interface Analysis, 27, 1055, 1999.

[10] P.J. Pearce, B. C. Ennis, I. Grabovac, C. E. M. Morris, Journal of Adhesion, 47 (1-3), 1994.

[11] S. S. Voyutskii, "Autohesion and Adhesion of High Polymers, Wiley Interscience, New York, 1963.

[12] D. R. Arnott, A. R. Wilson, P. J. Pearce, G. Mathys, M. R. Kindermann, A. Camilleri, "Void Development in Aerospace Film Adhesives During Vaccum Bag Cure", The International Aerospace Congress 1997, preprints of papers.

DISTRIBUTION LIST

The Effect of FM-73 Cure Temperature on the Durability of Bonded Joints Employing BR127 Primer

Andrew Rider and Peter Chalkley

AUSTRALIA

DEFENCE ORGANISATION

Task Sponsor
ASI4A
DGTA

S&T Program
Chief Defence Scientist
FAS Science Policy
AS Science Corporate Management
} shared copy
Counsellor Defence Science, London (Doc Data Sheet)
Counsellor Defence Science, Washington (Doc Data Sheet)
Scientific Adviser to MRDC Thailand (Doc Data Sheet)
Scientific Adviser Policy and Command
Navy Scientific Adviser (Doc Data Sheet and distribution list only)
Scientific Adviser - Army (Doc Data Sheet and distribution list only)
Air Force Scientific Adviser (Doc Data Sheet and distribution list only)
Director Trials

Aeronautical and Maritime Research Laboratory
Director
Chief of Airframes and Engines. Division
RLACS
Richard Chester
Peter Chalkley
Andrew Rider
Roger Vodicka
Richard Bartholomeusz
Ivan Stoyanovski

DSTO Library and Archives
Library Fishermans Bend (Doc Data sheet)
Library Maribyrnong(Doc Data sheet)
Library Salisbury (2 copies)
Australian Archives
Library, MOD, Pyrmont (Doc Data sheet)
US Defense Technical Information Center, 2 copies
UK Defence Research Information Centre, 2 copies
Canada Defence Scientific Information Service, 1 copy
NZ Defence Information Centre, 1 copy
National Library of Australia, 1 copy

Capability Systems Staff

Director General Maritime Development (Doc Data sheet)
Director General C31 Development (Doc Data sheet)
Director General Aerospace Development (Doc Data sheet)

Army

ASNSO ABCA, Puckapunyal, (4 copies)
SO(Science), DJFHQ(L), MILPO Enoggera, Queensland 4051 (Doc Data Sheet only)

Air Force

ASI-SRS

Intelligence Program

DGSTA Defence Intelligence Organisation
Manager, Information Centre, Defence Intelligence Organisation

Corporate Support Program

Library Manager, DLS-Canberra (Doc Data sheet)

UNIVERSITIES AND COLLEGES

Australian Defence Force Academy
- Library
- Head of Aerospace and Mechanical Engineering

Serials Section (M list), Deakin University Library, Geelong 3217
Hargrave Library, Monash University (Doc Data sheet)
Librarian, Flinders University

OTHER ORGANISATIONS

NASA (Canberra)
AusInfo

OUTSIDE AUSTRALIA

ABSTRACTING AND INFORMATION ORGANISATIONS

Library, Chemical Abstracts Reference Service (Doc Data sheet only)
Engineering Societies Library, US (Doc Data sheet only)
Materials Information, Cambridge Scientific Abstracts, US (Doc Data sheet only)
Documents Librarian, The Center for Research Libraries, US (Doc Data sheet only)

INFORMATION EXCHANGE AGREEMENT PARTNERS

Acquisitions Unit, Science Reference and Information Service, UK (Doc Data sheet only)
Library - Exchange Desk, National Institute of Standards and Technology, US (Doc Data sheet only)
National Aerospace Laboratory, Japan (Doc Data sheet only)
National Aerospace Laboratory, Netherlands (Doc Data sheet only)

SPARES (5 copies)

Total number of copies: 42

DEFENCE SCIENCE AND TECHNOLOGY ORGANISATION DOCUMENT CONTROL DATA	1. PRIVACY MARKING/CAVEAT (OF DOCUMENT)

2. TITLE	3. SECURITY CLASSIFICATION (FOR UNCLASSIFIED REPORTS THAT ARE LIMITED RELEASE USE (L) NEXT TO DOCUMENT CLASSIFICATION)
The Effect of FM-73 Cure Temperature on the Durability of Bonded Joints Employing BR127 Primer	Document (U) Title (U) Abstract (U)
4. AUTHOR(S)	5. CORPORATE AUTHOR
Andrew Rider and Peter Chalkley	Aeronautical and Maritime Research Laboratory PO Box 4331 Melbourne Vic 3001 Australia

6a. DSTO NUMBER	6b. AR NUMBER	6c. TYPE OF REPORT	7. DOCUMENT DATE
DSTO-TR-1057	AR-011-600	Technical Report	October 2000

8. FILE NUMBER	9. TASK NUMBER	10. TASK SPONSOR	11. NO. OF PAGES	12. NO. OF REFERENCES
M1/9/835	98/172	DGTA	22	12

13. URL on the World Wide Web	14. RELEASE AUTHORITY
http://www.dsto.defence.gov.au/corporate/reports/ DSTO-TR-1057.pdf	Chief, Air Operations Division

15. SECONDARY RELEASE STATEMENT OF THIS DOCUMENT

Approved for public release

OVERSEAS ENQUIRIES OUTSIDE STATED LIMITATIONS SHOULD BE REFERRED THROUGH DOCUMENT EXCHANGE, PO BOX 1500, SALISBURY, SA 5108

16. DELIBERATE ANNOUNCEMENT

No Limitations

17. CASUAL ANNOUNCEMENT Yes

18. DEFTEST DESCRIPTORS

adhesive bonding, bonded repair, composite materials

19. ABSTRACT

Bonded repairs to aircraft structure employing composite patches, may generate significant levels of residual stress in the repaired structure. This is due to the difference in the coefficient of thermal expansion between the repair material and the parent structure. One way of minimising the level of residual stress is to cure the repair adhesive at the lowest possible temperature. FM-73 is a fracture tough adhesive used in bonded repairs that is typically cured at 120°C for 1 hour. However, a cure cycle of 80°C for 8 hours may be employed in critical applications. The durability of bonds formed between aluminium and FM-73 epoxy adhesive using the two cure cycles mentioned has been examined. Al-2024 T3 unclad alloy was pretreated either using the RAAF standard gritblast and silane process or with the gritblast silane process followed by application of BR-127 chromate primer. Results suggest that whilst the addition of BR-127 primer improves bond durability for the adhesive cured at 120°C, there is little improvement observed for the adhesive cured at 80°C. Fracture analysis of failed wedge samples using SEM and surface analysis equipment indicate a change in the locus of fracture for the two cure cycles employed and a possible change in the fracture mechanism. Analysis of bonded samples in cross-section suggest that the interfacial region is wider for the 120°C cured sample. This result may suggest that processes such as interdiffusion of the primer and adhesive layers are important factors governing bond durability of adhesive joints.